Effect of Initial Size Distribution on Aerosol Coagulation

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The effect of particle coagulation on an aerosol with a truncated Junge initial size distribution was calculated for arbitrary particle size and time by obtaining an exact analytical solution to the Smoluchowski equation. The solution exhibits a crossover from the Junge form to an asymptotic exponential form. The persistence of a Junge-type size distribution for atmospheric aerosols and smoke aerosols is shown to be consistent with coagulation theory.

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Aerosols, which are suspensions of small particles (micron-size range) in gases, are unstable at high concentration: The particles collide as a result of Brownian motion and stick together. This coagulation process takes place in smoke,[1] in atmospheric aerosols,[2] and also in colloidal suspensions,[3] where the coagulation phenomenon was first studied theoretically by Smoluchowski.

The number distribution function, $n(v, t)$, with its dependence on particle volume v and time t, is the central quantity in coagulation theory. A solution for the time dependence of the number distribution was first obtained by Smoluchowski[3] in 1917 for a monodisperse initial size distribution. Subsequently, Schumann[4] obtained the result for an exponential initial distribution and Melzak,[5] Scott,[6] and Friedlander and Wang[7] obtained the result for a class of gamma distributions,

$$n(v, 0) = \frac{N_0 a^{p+1}}{v_2 p\,!}\left(\frac{v}{v_2}\right)^p \exp\left(\frac{-av}{v_2}\right), \tag{1}$$

in which N_0 is the total number concentration, p is a positive number that need not be an integer, and a and v_2 are constants.

While being of interest for various colloidal suspensions and specially prepared aerosols, neither these initial size distributions nor the distribution at later times are good approximations for such naturally occurring aerosols as atmospheric aerosols and combustion aerosols. Junge[8] found as the characteristic feature of atmospheric aerosols a $v^{-\beta}$ dependence of the size distribution with $\beta \approx 2$ for particles with diameters in the range 0.2–20 μm. Clark and Whitby[9] confirmed this dependence on particle size over the range 0.1 up to 3 μm, the maximum size measured, by a comprehensive study using an electrical aerosol analyzer and optical particle counter. This power-law dependence is manifest as a much broader size distribution than the exponentially steep distributions given by Eq. (1). Smoke aerosols have also been found to satisfy this power-law dependence[10] though the measurements are less complete in this case.

In this Letter, we report the solution of the coagulation equation for a truncated Junge initial distribution,

$$n(v, 0) = ae^{-v/b}/(v+c)^2. \tag{2}$$

This distribution is in qualitative agreement with the observed size distribution of atmospheric aerosols and smoke aerosols. The characteristic $v^{-\beta}$ dependence of the size distribution is represented in Eq. (2) with the exponent β set equal to 2 and the constants b and c determining the size range over which the power-law behavior persists. The experimentally observed rapid drop off in the size distribution for large particle sizes, particle diameter of 20 μm and greater, which is presumably caused by particle settling, is accounted for in Eq. (2) by the exponential term. The constant c is introduced to keep the size distribution finite at small particle sizes, which is a difficult region to characterize experimentally and is highly dependent on local sources and weather conditions for atmospheric aerosols.[9]

The time evolution of coagulating particles is described by the Smoluchowski equation

$$\partial n(v, t)/\partial t = \int_0^v \Gamma(v - v', v')n(v - v', t)n(v', t)dv' - 2n(v, t)\int_0^\infty \Gamma(v, v')n(v', t)dv', \tag{3}$$

where $n(v, t)dv$ is the number concentration in the particle volume size range v to $v+dv$ and $\Gamma(v, v')$ is the coagulation frequency, taken as constant in this analysis. A general mathematical survey of the coagulation equation is given by Drake.[11]

The solution of Eq. 3 for the initial condition given by Eq. (2) is given in terms of the reduced number distribution θ, reduced particle size $\tilde{v}$, and the timelike coagulation parameter λ:

$$\theta(\tilde{v},\lambda)=e^{-c\tilde{v}/b}\int_0^\infty \frac{e^{-x\tilde{v}}xe^{-x}\,dx}{\{1-\lambda[1-xe^{-x}\mathrm{Ei}(x)]\}^2+[\pi\lambda xe^{x}]^2},\quad \lambda<1; \tag{4a}$$

$$\theta(\tilde{v},\lambda)=(4a)+\frac{e^{-c\tilde{v}/b}\exp(x_0\tilde{v})}{\lambda^2[(1+x_0)e^{x_0}E_1(x_0)-1]},\quad \lambda>1; \tag{4b}$$

where E_1, E_2, and Ei are the standard exponential integrals and where x_0 is the root of the equation,

$$1-\lambda[1-x_0e^{x_0}E_1(x_0)]=0.$$

The reduced variables $\theta, \tilde{v}$, and λ are related to the physical variables n, v, and t and the initial number concentration, N_0:

$$\theta=[n(v,t)/(1-\lambda)^2]\,c^2/a,\quad \tilde{v}=v/c,$$

$$\lambda=\Gamma N_0t/[(1+\Gamma N_0t)\exp(c/b)E_2(c/b)]. \tag{5}$$

The solution given in Eqs. (4) and (5) was obtained by the Laplace-transform technique, which has been used previously by others[5-7] for the gamma initial distribution. The Laplace transform for the truncated Junge initial distribution has fundamentally different analytic behavior compared with the gamma initial distribution in that it contains both a pole and a branch point in the complex plane while the gamma distribution only has poles. The branch point arises from the logarithmic singularity in the Laplace transform of the initial distribution, and the branch cut integration around the singularity is the integral in Eq. (4). For large v the integral is proportional to the initial distribution and thus there is a memory effect. Junge[12] previously discussed this memory effect on the basis of a numerical calculation for a specific initial size distribution.

For a Junge-type distribution without exponential cutoff, Mulholland, Lee, and Baum[10] have shown that the branch cut integral is the dominant contribution for large v. However, with the exponential cutoff included, for $\lambda>1$ there is also a contribution from a pole at x_0, which is the source of the second term in Eq. (4). Eventually, for λ sufficiently close to

$$\lambda_\infty=[\exp(c/b)E_2(c/b)]^{-1},$$

the pole contribution dominates with the asymptotic result

$$n(v,t)\sim[N(t)^2/V]\exp[-vN(t)/V]. \tag{6}$$

Here $N(t)$ is the total number concentration at time t and V is the total volume concentration of the aerosol. This asymptotic result is identical to the asymptotic result obtained by Friedlander and Wang for the gamma distribution with the order p equal to an integer. More generally, Lushnikov[13] has shown that for $n(v,t=0)\leq Ae^{-Bv}$ the long-time asymptotic size distribution is independent of the detailed form of the initial distribution and is identical with Eq. (6). However, no estimate as to how much time must pass before this result is applicable is given. This information is of crucial importance, as will be demonstrated below.

The aging of a truncated Junge initial-distribution aerosol can be divided into time domains by the coagulation parameter λ. For $\lambda<1$ the memory of the initial distribution predominates, while for $\lambda>1$ the size distribution begins to approach the asymptotic form of Eq. (6). It can be shown that for $c/b\ll1$, which is the case of interest for smoke and atmospheric aerosols, the crossover condition at $\lambda=1$ corresponds to particle growth by coagulation to the extent that the average particle volume is of the same order as the exponential volume parameter b. In Fig. 1 the size distribution is plotted for $c/b=10^{-3}$ and for a range of values of the coagulation parameter λ. For $\lambda<1$ it is seen that the size distribution approaches the initial distribution for large particle size while for $\lambda>1$ this is not the case.

It is of interest to calculate the actual time at which the memory of the initial distribution is lost for physically interesting initial size distributions. For an initial total number concentration, N_0, equal to the average for the Los Angeles smog experiment,[14] 1×10^5 particles/cm^3, a coagulation coefficient, $\Gamma=10^{-9}$ cm^3/s for 0.1-μm colliding spheres,[15] and c/b $(=10^{-6})$ chosen to give v^{-2} dependence over six decades in particle volume (two decades in particle diameter), the time at which $\lambda=1$ is found from Eq. (6) to be 2.4 years. Since the lifetime of atmospheric aerosols is on the order of 8 d,[16] one would not expect to observe the transition to the exponential behavior but rather only observe the memory effect of the initial distribution. Of course, for a quantitative study even for eight days one must consider the effects of the mixing in of new aerosol, settling, condensation of vapor on the aerosol, and evapo-

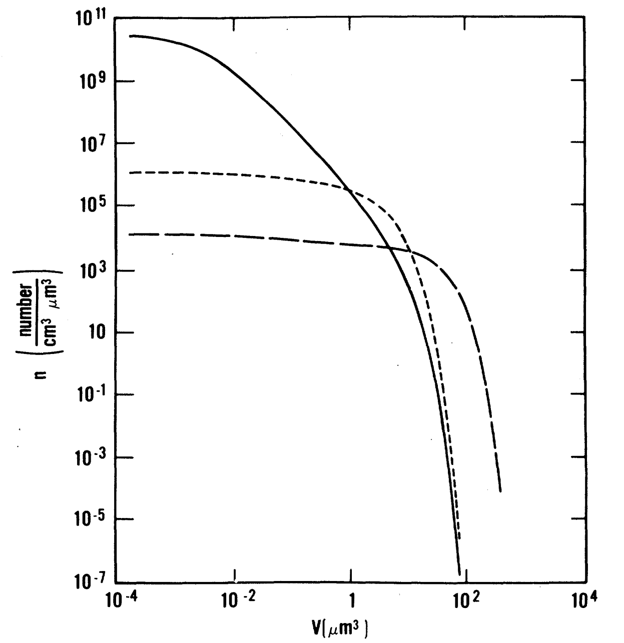

FIG. 1. The size distribution is plotted in a log-log form for $\lambda = 0$, $\Gamma N_0 t = 0$ (solid line); $\lambda = 0.9964$, $\Gamma N_0 t = 10^2$ (short dashes); and $\lambda = 1.0026$, $\Gamma N_0 t = 10^3$ (by dashes). The initial distribution parameters ($c/b = 10^{-3}$, $a = 3.4 \times 10^5\ \mu m^3/cm^3$, $c = 3.4 \times 10^{-3}\ \mu m^3$) were chosen to give good agreement with the observed size distribution of a "fresh" smoke aerosol.

ration of the aerosol.

For an initial smoke-aerosol concentration of 3×10^6 particles/cm^3,[17] which is approximately the alarm threshold concentration for smoke detectors, and for c/b ($= 10^{-3}$) chosen to give v^{-2} dependence over three decades in particle volume, the time at which $\lambda = 1$ is on the order of 14 h. This is obviously far in excess of desirable smoke detector alarm times. While a more manageable time scale than the atmospheric case, there are experimental difficulties in observing smoke coagulation over a period of 14 h because of particle diffusion to the walls and particle settling. So again the memory effect of the initial distribution plays a dominant role.

The time estimates made above are based on a constant collision frequency Γ, while in reality Γ is a function of the sizes of the colliding particles. We expect that the memory of the initial distribution is a general feature of the coagulation equation for initial distributions such as the truncated Junge and the magnitude of the memory time will be affected by the form of Γ but the existence of the memory effect will not. The fact that the measured size distributions of atmospheric aerosols and smoke aerosols have a truncated Junge form is consistent with the existence of a memory effect for coagulating aerosols with a size dependent Γ. In fact, we feel that this memory effect provides a possible explanation for the discrepancy discussed by Hidy and Brock[18] between the measured size distribution for atmospheric aerosols and the predicted behavior based on a similarity and therefore in effect a long-time solution of the coagulation equation with size-dependent Γ.

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